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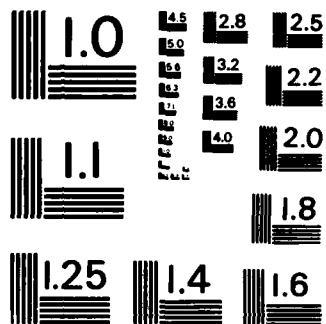
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Research Report

OPTOACOUSTIC SPECTROSCOPY

Andrew C. Tam

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Optoacoustic Spectroscopy

by

A. C. Tam

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OPTOACOUSTIC SPECTROSCOPY

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ABSTRACT: The technique of optoacoustic spectroscopy relies on the use of modulated or pulsed light beams to produce, directly or indirectly, acoustic waves or pulses in a gaseous or condensed sample; as the excitation beam is scanned in wavelength, an excitation spectrum, called optoacoustic (or photoacoustic) spectrum, is produced. This paper reviews some of the theories and experiments in this field.

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1. INTRODUCTION

The opto-acoustic (OA) or photo-acoustic (PA) effect may be described as the "splashing" of photons in matter, that is, the generation of acoustic waves by electromagnetic waves or other types of radiation incident on a sample. This effect was discovered by A. G. Bell in 1880, who observed that audible sound is produced when chopped sunlight is absorbed at a surface. Although the OA effect has been known for over 100 years, there has been a recent resurgence of interest in the phenomenon, both in theoretical and experimental studies. This renewed interest stems from several possible reasons. Intense light sources, such as lasers and arc lamps, are more readily available. High sensitivity detection tools for measuring acoustic waves have been developed. OA techniques have been shown to be capable of detecting weak absorption features (*e.g.*, due to trace contaminants) in gases as well as in condensed matter. Furthermore, OA methods are finding many unique applications, such as in spectroscopic studies of opaque or powdered materials, studies of energy conversion processes, and nondestructive evaluation or imaging of invisible subsurface defects in solids.

The essential features of OA spectroscopy is that the heat deposited in the sample by the *absorption* of a modulated light beam is detected. Thus, OA spectroscopy has the following advantages. (a) It is a zero background method, unlike conventional extinction measurements; (b) It can be used for strongly light-scattering materials; (c) The OA signal is dependent on the excited-state decay pathways resulting in acoustic generation. These features distinguish OA spectroscopy from other spectroscopic methods. In this article, we shall examine OA generation processes, discuss the acoustic detection methods, and review the spectroscopic applications in

gases and in condensed matter. This article is meant to cover the important points relevant to analytical application of lasers, but not to be an in-depth review. Detailed reviews of spectroscopic and non-spectroscopic applications of OA techniques have been given, for example, by Pao (1), Rosencwaig (2), Coufal *et al.* (3), Patel and Tam (4), and Tam (5).

2. OPTOACOUSTIC GENERATION

OA generation can be due to diversified processes. Some of the possible OA generation mechanisms are shown in Fig. 1, where the OA generation efficiency η (*i.e.*, acoustic energy generated/light energy absorbed) generally increases downward for the mechanisms listed. For electrostriction or thermal expansion mechanisms, η is small, for example on the order of 10^{-12} to 10^{-8} , while for breakdown mechanisms, η can be as large as 0.3, as reported by Teslenko (6). However, generally it is only the thermal expansion mechanism that is useful for the purpose of spectroscopy, and further discussions are limited to this so-called "thermal-elastic" OA generation, which can be grouped into two general cases: direct and indirect. In the direct thermal OA generation, treated in detail by numerous workers including White (7), Gourney (8), Hu (9), Liu (10), Lai and Young (11), Heritier (12), and Sullivan and Tam (13), the modulated excitation beam produces a time-dependent heating of the sample, and thus an acoustic wave in it. In the indirect OA generation, treated by Rosencwaig and Gersho (14), Adamodt and Murphy (15), Wetsel and McDonald (16), Tam and Wong (17), and others, the excitation beam produces a modulated temperature at the surface of a solid or liquid sample which is in contact with a transparent coupling fluid (typically a gas); thus time-dependent expansion of the coupling fluid is produced, and this pressure wave can be sensed by a microphone. Both direct and indirect OA

generation are widely used for spectroscopic purposes. Indirect OA generation is frequently called "photo-acoustic" (PA) generation in the literature, and we shall use the name PA here to indicate indirect OA generation involving heat coupling to a transparent fluid adjacent to a sample.

2.1 Simple Theory for Direct OA Generation

The detailed general theories of OA generation tend to be rather involved; to show the important parameters, we consider a simple case of direct and of indirect OA generation.

The simplest case of direct thermal OA generation is indicated in Fig. 2a, for the case of an infinite weakly-absorbing medium excited by a narrow collimated pulsed laser beam of radius R_s . We assume that the laser pulse width τ_L is sufficiently short so that thermal diffusion effects can be neglected. The initial expansion ΔR_s of the source radius R_s immediately after the laser pulse is given by

$$\pi(R_s + \Delta R_s)^2 l - \pi R_s^2 l = \beta V \Delta T \quad (1)$$

with the initial temperature rise

$$\Delta T = \frac{E \alpha l}{\rho V C_p} \quad (2)$$

where l is the length of the OA source (assumed long), β is the expansion coefficient, $V = \pi R_s^2 l$ is the source volume, E is the laser pulse energy, α is the absorption length (with $\alpha l \ll 1$), ρ is the density and C_p is the specific heat at constant pressure. Combining Eqs. (1) and (2) and assuming $\Delta R_s \ll R_s$ (true in all cases we are considering), we have

$$\Delta R_s = \frac{\beta E \alpha}{2\pi R_s \rho C_p} \quad (3)$$

which has been given, for example, by Patel and Tam (4). The peak displacement $U(r)$ at the observation point at distance r from the OA source (for $r \ll l$) varies as $r^{1/2}$ because of conservation of acoustic energy, as described by Landau and Lifshitz (18) for a cylindrical acoustic wave:

$$U(r) = \Delta R_s (R_s/r)^{1/2} = \frac{\beta E \alpha}{2\pi R_s^{1/2} \rho C_p r^{1/2}} \quad (4)$$

The peak acoustic pressure $P(r)$ at position r is related to the acoustic displacement $U(r)$ and sound velocity c by

$$P(r) \approx c \rho U(r) / \tau_L \quad (5)$$

Substituting Eq. (4) into (5), we obtain the peak OA pressure observed at r for small source radius as

$$P(r) \approx \frac{\beta c E \alpha}{2\pi R_s^{1/2} C_p \tau_L r^{1/2}} \quad (6)$$

Equation (6) is a basis for OA spectroscopy based on direct OA generation. It indicates that the normalized OA signal, defined as the detected acoustic pressure amplitude P divided by the laser pulse energy E , is proportional to the absorption coefficient α , with a proportionality constant K that depends on geometry and thermo-elastic properties. Thus, if the laser beam is tunable, the normalized OA spectrum provides an uncalibrated absorption spectrum if K is unknown. Absolute calibration is possible by evaluating $K = \beta c / (2\pi R_s^{1/2} C_p \tau_L r^{1/2})$, or more practically, by measuring the normalized OA signal for a known absorber at one wavelength and thus

empirically finding K . Equation (6) also indicates clearly the advantages and features of OA spectroscopy of weak absorption by direct OA generation. This method is zero-background, since $P \rightarrow 0$ if $\alpha \rightarrow 0$. For detecting small α , the signal magnitude P is increased by using intense laser pulses. Equation (6) indicates that the OA generation efficiency η defined earlier is proportional to the laser intensity; this does not violate energy conservation, since small absorption approximation is assumed here. Although the treatment here is semiquantitative for the simplest case, more detailed theories (e.g., done by Patel and Tam (4)) gave essentially the same conclusions.

2.2 Simple Theory for Indirect OA Generation

A simple case of PA generation is indicated in Fig. 2b. In general, PA generation does not provide as high a sensitivity as the direct OA generation for detecting weak absorptions, basically because it is only a thin layer of the thickness of a thermal diffusion length at the surface of the solid sample that is thermally coupled to the gas, producing the detected acoustic wave. However, PA generation is very valuable for the opposite case of weak absorption, *i.e.*, when the optical absorption is so strong that no light passes through the sample and hence conventional transmission monitoring fails. This case is illustrated in Fig. 2b. The mathematics can be semi-quantitatively described as follows, and more detailed mathematical treatment has been given by Rosencwaig and Gersho (14).

Let the incident laser beam of radius r and modulated at frequency f be incident on the sample of thickness l_s in a cylindrical cell of radius R and coupling gas thickness l_g . Let the sample optical attenuation coefficient be α at the excitation wavelength, and the optical absorption length be $\mu_a = 1/\alpha$. The modulated component of the laser-induced heating is distributed over a diffusion length μ_s given by

$$\mu_s = [D_s/(\pi f)]^{1/2} \quad (7)$$

when D_s is the thermal diffusivity of the sample. We assume that the optical wavelength and the modulation frequency are chosen so that the lengths ℓ_g , μ_a , and μ_s are in decreasing magnitudes. This represents one of the most interesting cases for OA spectroscopy. Let the modulated laser beam intensity that is absorbed by the sample be represented by

$$I(t) = \frac{1}{2} I_0 (1 + \sin 2\pi f t) \quad (8)$$

The modulated heat produced within the diffusion length μ_s is only a fraction μ_s/μ_a of the power input I_0 which is absorbed over a depth μ_a . The concept of heat conduction applied to the geometry of Fig. 2b can be written as follows:

$$(\text{thermal conductivity}) \times (\text{thermal gradient}) \quad (9)$$

$$= (\text{thermal power within diffusion length})$$

which means

$$k_s(\theta_0/\mu_s) \approx I_0(\mu_s/\mu_a) \quad (10)$$

where k_s is the sample conductivity and θ_0 is the amplitude of the temperature variation on the sample surface, which is thermally coupled to an active volume V_{act} of the gas, given by

$$V_{act} \approx \pi r^2 \mu_g \quad (\text{for } \ell_g > \mu_g), \quad (11)$$

where μ_g is the gas thermal diffusion length. Using the ideal-gas law, the amplitude δV of the volume change of V_{act} is

$$\delta V = V_{\text{act}} \theta_0 / T, \quad (12)$$

where T is the absolute temperature. Now the volume fluctuation δV causes a pressure fluctuation δP at the microphone. Assuming the adiabatic pressure-volume relation, we have

$$\delta P = \gamma P \delta V / V, \quad (13)$$

where γ is the ratio of the specific heats and V is the total cell volume, given by

$$V = \pi R^2 \ell_g. \quad (14)$$

Combining Eqs. (10)-(14), we obtain the PA amplitude δP as

$$\delta P \approx \frac{\gamma P \mu_g \mu_s^2 I_0 r^2}{\mu_a k_s \ell_g T R^2} \quad (15)$$

Eq. (15), which agree with the more detailed work of Rosencwaig and Gersho (14), indicates that the PA magnitude is proportional to the sample absorption coefficient $\alpha = 1/\mu_a$, and the normalized PA signal $\delta P/I_0$ measured for a range of excitation wavelength λ can provide the absorption spectrum $\alpha(\lambda)$ as in the direct OA generation case. The unusual advantage here is that spectra of totally opaque or highly light-scattering materials can now be measured.

3. DETECTION

3.1 Microphones

The sound transducer used in a gas-phase OA cell (whether it is a gaseous sample that is being studied, or a condensed matter sample studied via the PA generation process monitored in a coupling gas) is usually a commercial microphone, which is typically a capacitance sensor that senses the deflection of a diaphragm in contact with

the gases. Electrets and piezoelectric microphones are also sometimes used by researchers. Many commercial brands are available, and the choice should depend on the best compromise among sensitivity desired, bandwidth, size, and noise. Sensitivity as high as ~ 100 mV/Pascal is available in commercial microphones (e.g., produced by Bruel and Kjaer), and bandwidth ~ 100 kHz is also available; however, high sensitivity is usually available only as a trade-off for lower bandwidths and larger microphone size. Exotic "microphones" are also available. For example, Miles *et al.* (19) have described a thin-filament device that "follows" the gas flows and can be used for measuring the small pressure fluctuations in OA spectroscopy. Also, Choi and Diebold (20) have developed a "laser Schlieren microphone" which relies on the use of a "probe laser" to monitor the deflection of a diaphragm due to the pressure modulation in an OA cell.

3.2 Piezoelectric Transducers

For detecting the direct OA signal produced in condensed matter, microphones are typically not suitable because of the serious acoustic impedance mismatch at the sample-gas interface which means that typically, less than 10^{-4} of the acoustic pressure amplitude are transmitted from a solid sample into a coupling gas. Piezoelectric ceramic materials are more suitable for detecting the direct OA signal in condensed matter. Many types of piezoelectric ceramics or crystals are commercially available, e.g., lead zirconate titanate (PZT), lead metaniobate, lithium niobate, crystalline quartz, etc, and reviews on these transducers are given by Mason and Thurston (21). For OA detection, the piezoelectric element with metallized electrodes should be mounted in a suitable manner. One way of mounting is described by Patel and Tam (4). A PZT cylinder (PZT 5A from Vernitron, Ohio) of 4 mm diameter and 4 mm height is pressed against a front stainless steel diaphragm that is polished on both sides. The PZT

element is enclosed in the stainless steel casing so that the following noise sources are minimized: electromagnetic pick-up, possible corrosion due to contact with reactive samples and absorption of stray light that is scattered towards the transducer. The sensitivity of such a PZT transducer is typically ~ 3 V/atm. This is much smaller than that of a sensitive microphone (e.g., B&K model 4166) with a sensitivity $\sim 5 \times 10^3$ V/atm. However, PZT transducers are preferred for OA detection in condensed matter because of the much faster risetimes and better acoustic impedance matching for PZT compared to microphones.

Thin polymeric films that are made piezoelectric are also frequently used for OA monitoring in condensed matter. These are highly insulating polymeric films that can be poled in a strong electric field at elevated temperatures or can be subjected to charged-beam bombardment so that they become polarized and exhibit piezoelectric character. Such films include polyvinylidene difluoride (PVF₂), teflon, mylar, etc., with PVF₂ being the most commonly used. There is strong interest in the use of PVF₂ film as transducers for acoustic imaging in the human body because of the non-ringing characteristic of the film (Q is much lower than PZT), fast risetime, flexibility, and good acoustic impedance matching to liquids like water. A disadvantage of PVF₂ is that its sensitivity is typically much lower than PZT. Many ways to mount a PVF₂ film are possible, and a way is described by Bui *et al.* (22). Tam and Coufal (23) have shown that such a PVF₂ transducer is capable of ringing-free detection of OA pulses with widths ~ 10 nsec excited by a pulsed N₂ laser.

3.3 Other Types of Transducers

Other types of transducers for detecting pulsed acoustic signal have been described in the literature. For example, Dewhurst and co-workers (24-25) have used

capacitance transducers for detection of OA pulses generated in metallic samples by pulsed Nd:YAG lasers. Amer and co-workers (26) have used a continuous probe laser beam directed at the sample surface to detect the surface distortions due to the thermal or acoustic effects excited by a pulsed laser. Tam *et al.* (27,28) have used a continuous probe laser beam to detect the transient refractive index profile of the OA pulse in gases as well as in liquids; such acoustic refractive index profile causes the probe beam to undergo a transient deflection proportional to the spatial derivative of the refractive index.

The methods of optical probing of OA surface distortions or refractive index changes represent a class of non-contact transducers. There are many cases where noncontact or remote OA monitoring are necessary, as in the case of an inaccessible sample (*e.g.*, in a vacuum chamber), or for samples in hostile environments, or samples that cannot be contaminated. A good example is the OA spectroscopy of free radicals like OH in flames, as performed by Gupta and co-workers (29). In their work, they used a tunable pulsed ultraviolet laser beam to excite OH free radicals in a methane-oxygen flame and used a continuous HeNe probe beam to detect the thermal as well as acoustic refractive index gradient caused by a laser pulse of 1 μ sec duration. Their work clearly indicates that totally non-contact OA spectroscopy can be performed in a localized region in a highly hostile environment. Besides spectroscopy, flame temperature profiles can also be obtained by monitoring the acoustic speeds, as shown earlier by Zapka *et al.* (30).

3.4 Absorption Modulation and the OA Cell

OA generation requires a modulated absorption which can be obtained from a modulated light beam or modulated absorption characteristics of the sample.

Modulation methods for the light source include Q-switching, mode-locking, flash-lamp pulsing, wavelength-switching, and the use of mechanical modulators (choppers), electro-optic modulators, acousto-optic modulators, wavelength-modulating devices, *etc.* Modulation of the absorption characteristics of the sample is possible for example, by applying modulated magnetic or electric fields to the sample; thus, Kavaya *et al.* (31) have demonstrated that Stark modulation of gas sample by a modulated electric field is excellent for OA detection because the background signal in the Stark modulation mode is about 500 times smaller than that in the same OA cell in the conventional chopped light beam mode. This is because the background absorption (*e.g.*, due to the cell windows or due to the buffer gases) has little dependence on the electric field. In a sense, the Stark modulation method is equivalent to a wavelength modulation method, as is done by Lahmann *et al.* (32) for OA studies of liquids. Castleden *et al.* (33) have described a simple wavelength modulated PA spectrometer, which generates differentiated PA spectra: this provides an apparent enhancement in the resolution, and results in an increased precision of locating absorption features in the sample.

The OA cell is a container for the sample and the microphone or transducer, such that the incident excitation beam can be absorbed by the sample to produce an acoustic signal. At low enough modulation frequencies or long enough pulse durations of the excitation beam, the exact geometry of the OA cell is important, since the acoustic wave is reflected from the cell walls, and acoustic interference and resonances can occur. Indeed, many researchers, *e.g.*, Hess (34), have exploited the effect of acoustic resonance to enhance the OA detection sensitivity. However, at very high modulation frequency or for very short pulse duration of the excitation beam, effects of reflections

from cell walls are unimportant, and so is the geometry of the OA cell; indeed, "leaky" OA cell can be used in such cases.

The above design considerations for an OA cell are aimed at two factors: minimizing noise (*i.e.*, spurious signal) and maximizing signal. Further useful design considerations include the use of Brewster windows for minimizing light scattering, multipassing for increased sensitivity, recessed microphone for avoiding scattered light onto it, acoustic baffles and shields for reducing effects of unwanted acoustic sources, and locating the excitation beam entrance and exit positions at acoustic nodes in a resonant cell.

4. OA SPECTROSCOPY IN GASES

Modern interest in OA spectroscopic detection in gases begins with the work of Kreuzer (35) in 1971, who reported a detection sensitivity of 10 parts per billion of methane in air, using a 0.015 watt infrared laser for excitation; Kreuzer also indicated that a more powerful infrared laser source may make possible 0.1 part per trillion impurity detection. This work stimulates many later experiments for achieving high OA detection sensitivity in various gases. The sensitivity of laser OA detection in gases has now advanced to an absorption measurement capacity of $\sim 10^{-10} \text{ cm}^{-1}$ with a cell length of $\sim 10 \text{ cm}$ (see Patel and Kerl (36)). This high sensitivity cannot be matched by other conventional absorption techniques like extinction measurement, which includes absorption plus all scattering losses, and cannot be readily used to monitor absorption coefficients less than $\sim 10^{-3} \text{ cm}^{-1}$. There are a few other ultrasensitive techniques for spectroscopic detection that may have sensitivities better than the laser OA technique, notably the single atom detection method of Hurst *et al.* (37) using multistep laser excitation and ionization, and also luminescence monitoring with pulsed laser

excitation. Although the laser OA method lags behind the multiphoton ionization spectroscopy or the luminescence monitoring spectroscopy method in sensitivity, it does offer other advantages over these other methods like simplicity and suitability for atmospheric conditions. The simplicity of laser OA detection means that only a sound transducer is required. The suitability for atmospheric conditions means that nonradiative thermal relaxation in a high density gas system occurs very generally (may be only partial in certain highly fluorescent or chemically active system), while ion-attachment, diffusion, recombinations, and quenching phenomena may pose serious limits to the other detection techniques.

4.1 Weak One-Photon Absorptions

The high detection sensitivity of a laser OA method has the obvious use for detecting very weak absorptions, such as those that are forbidden by dipole selection rule or by spin conservation. An example is an overtone vibrational transition. If the vibrational potential of the molecule can be represented by a simple harmonic oscillator potential, only the fundamental vibrational excitation is allowed for optical absorption, and all higher harmonics have zero dipole matrix elements. However, in a real molecule, higher harmonic transitions are possible because the potential well is at least slightly anharmonic. The use of dye laser OA spectroscopy to examine overtone absorption in gases was demonstrated by Stella *et al.* (38). In their experiment, the 6190Å overtone absorption band of CH₄ and 6450Å overtone absorption band of NH₃ was measured by placing the OA cell in the cavity of a dye laser and scanning the laser across the absorption band. They were able to resolve rotational features. Subsequently, numerous researchers have performed intracavity laser OA spectroscopy

for measuring weak overtone vibrational absorptions in molecules, *e.g.*, Bray and Berry (39), Smith and Gelfand (40), and Fang and Swofford (41).

4.2 Trace Detection

The high sensitivity of laser OA detection also permits measurements of weak absorptions due to a strong absorption line of a trace constituent. The idea of trace detection by "spectrophone" detection in conjunction with laser excitations was first demonstrated by Kerr and Atwood (42), and the later work of Kreuzer (35) greatly enhance the interest. Patel (43) reported some pioneering work of laser OA monitoring of pollutants. His light source is a spin-flip Raman laser (SFRL) with InSb as the active medium that is pumped by a CO or CO₂ laser. The IR output from the SFRL is tunable by a magnetic field, which is typically a superconducting magnet situated in the same liquid helium dewar as the InSb crystal. The detection technique turns out to be extremely useful for in-situ pollutant detection, both in terrestrial stations or in upper atmosphere. Many other workers have recently demonstrated outstanding successes in detecting trace pollutants in nitrogen or in atmospheric air. Angus *et al.* (44) have reported OA detection of 10 ppb of NO₂ using a modulated cw dye laser excitation. Clapsy *et al.* (45) reported a study of laser OA detection of explosive vapors, including nitroglycerine, ethylene glycol dinitrate, and dinitrotoluene. A CO₂ laser source tuned to suitable lines in the 9 μm to 11 μm spectral range is used to minimize background absorption due to other normal constituents in air. Koch and Lahmann (46) have used a cw frequency-doubled dye laser of 1W power to detect SO₂ of concentrations as low as 0.1 ppb. Vansteenkiste *et al.* (47) have reported the use of a PbS_{1-x}Se_x diode laser of 96 μW power at 4.8 μm to detect the absorption of CO in a small nonresonant OA cell. A concentration of 50 ppm of CO in N₂ can be detected by operating the cell in a

double pass mode. Gerlach and Amer (48) have earlier reported a detection of 0.15 ppm of CO by using a higher power laser.

4.3 Detection of Excited States

Since trace amount of excited states can be produced in a gaseous system by suitable excitation mechanisms (optical, discharge, chemical, *etc.*), it is logical to expect OA detection method to be well suited for measuring excited state spectra and collision dynamics. This is first demonstrated by Patel *et al.* (49) for a gaseous system of NO, that is, step-wise excited by two infrared lasers. Also, chemically reactive gases may produce transient intermediate chemical species, and the high sensitivity available with OA detection may be useful to identify some of the intermediate products, and hence provide important understanding of the reaction channel. In continuous photolysis, concurrent spectroscopic identification of photolysis products is generally very difficult since the steady-state concentration of intermediates is usually too small for spectroscopic measurements without using a matrix isolation procedure. Colles *et al.* (50) have shown that in a gas phase continuous photolysis experiment, OA detection of intermediates is possible using a tunable dye laser.

4.4 Nonlinear Optical Absorptions

The high-sensitivity OA method is also ideally suited for measuring nonlinear absorption or nonlinear optical scattering effects, since some degree of heat deposition (often small amounts) in the gas usually occurs due to these nonlinear optical interactions, *e.g.*, Raman gain spectroscopy, Doppler-free saturation spectroscopy, and multiphoton absorption spectroscopy.

Photoacoustic Raman-gain spectroscopy (PARS) was first suggested by Nechaev and Ponomarev (51), and was first observed by Barrett and Berry (52) in gases. In their experiments, the pump beam was a continuous Ar^+ laser beam chopped at 573 Hz, and the signal beam was a continuous dye laser beam tuned near the 6054\AA of CH_4 . With microphone detection, the symmetric stretch vibrational mode of methane near 2900 cm^{-1} was detected as a PARS signal when the photon energy difference of the two laser beams is resonant with this Raman mode. In the more recent experiments on PARS, West and Barrett (53) reported that greatly enhanced sensitivity can be obtained using pulsed lasers for the pump and probe beams.

The OA spectroscopy performed so far are mostly of resolution at best equal to the Doppler width. In principle, the high sensitivity of detection implies that the technique of saturation spectroscopy (already shown for fluorescence monitoring, absorption monitoring or optogalvanic monitoring) can be used with OA monitoring to allow a Doppler-free linewidth, *i.e.*, with the spectra linewidth being limited by the molecular lifetimes. This is demonstrated by the experiment of Marinero and Stuke (54). In their work, the P(193) line of 11-0 band of the B \rightarrow X transition of I_2 is measured using a single-longitudinal-mode cw dye laser beam which is split into two opposite beams chopped at $f_1=757\text{ Hz}$ and $f_2=454\text{ Hz}$. The OA signal is observed to contain a sum modulation frequency component (*i.e.*, at f_1+f_2) when the dye laser is within the natural linewidth of an absorption line.

5. OA SPECTROSCOPY OF CONDENSED MATTER

5.1 Indirect OA Generation

The earlier work in condensed matter generally involved indirect OA generation (referred to here as PA spectroscopy). For example, Harshbarger and Robin (55), and

Rosencwaig (56) simply extended the gas-phase OA spectroscopy technique of Kreuzer (35) to solids, namely they used a gas-phase microphone to sense the heating and cooling of a thin gas layer in contact with the sample illuminated by a chopped light beam. This gas-phase-microphone PA technique for condensed matter relies on the inefficient thermal diffusion in the sample and in the coupling gas: hence, this technique lacks sensitivity, and is typically useful only for optical absorptions larger than 1%. However, an essential advantage of PA spectroscopy is that many types of "difficult" samples can be measured without any "sample preparation," as would be required by conventional transmission-monitoring methods. In the review by Rosencwaig (2), it is well documented that PA spectra can be obtained for highly light-scattering and/or opaque materials like powders, pigments, polymers, catalysts, hemoproteins, plant matter, bacteria, *in-vivo* cells, and so on. However, to obtain a meaningful PA spectrum, two precautions are required: avoid "PA saturation," and minimize light scattering onto any absorbing surface of the PA cell and especially of the microphone.

The phenomenon of PA saturation is well recognized, and is explained in detail by Rosenwaig and Gersho (14) and others. The intuitive explanation of PA saturation (already implied in Eq. (10)) for a totally opaque sample with wavelength-dependent absorption length μ_a is as follows. Suppose the laser modulation frequency f is high enough so that the sample thermal diffusion length μ_s (see Eq. (7)) is shorter than μ_a throughout the wavelength range of interest. In this case, at each wavelength, λ , the effective heat $H(\lambda)$ is $I_0\mu_s/\mu_a$, since the incident light amplitude $I_0(\lambda)$ is absorbed in a thickness μ_a but only a thinner layer of thickness μ_s can communicate with the coupling gas and hence contribute to the PA signal. Hence, we see that $H(\lambda)$ is

proportional to the absorption coefficient $\alpha(\lambda)$ and hence the PA signal magnitude is linear to $\alpha(\lambda)$. This is nonsaturation. However, if the modulation frequency f is decreased so that μ_s is equal to μ_a at a certain wavelength λ_1 , the heat $H(\lambda_1)$ is now equal to $I_0(\lambda_1)$, since all the heat generated in the depth μ_a at this wavelength can communicate with the coupling gas. This indicates that $H(\lambda_1)$ has reached the maximum value $I_0(\lambda_1)$, independent of $\alpha(\lambda_1)$. Thus, PA saturation has occurred. A way to avoid PA saturation for opaque samples is to make sure that the modulation frequency is large enough.

The second precaution mentioned earlier is the minimization of light-scattering causing spurious signal generation at cell walls or microphase surfaces. One way to minimize this is to use a PA cell with a narrow passage connecting the sample and the microphone, as done by McClelland and Kniseley (57), Monahan and Nolle (58), Aamodt and Murphy (15), Bechthold *et al.* (59), and others. The passage can serve several purposes: (a) Light scattering from the sample, sample holder, and window onto the microphone is reduced. (b) By varying the volume of the sample or the microphone chamber, Helmholtz resonance can be obtained, thus enhancing the PA signal. (c) By using a long enough connection passage, the sample chamber can be kept at a very cold or very hot temperature to perform PA spectroscopy at these temperatures with the microphone being kept at room temperature.

The optical absorptions by aerosols, colloids, powders, and all other form of particulates provide good examples of the applicability of PA methods because conventional methods work poorly at best. Absorptions due to fine particles is very important to measure, both in basic science and in applied technologies like the motor industry, smog control, pigment manufacturing, coal conversions, *etc.* The PA

absorption measurements of powders using gas-coupling methods have been reported by several authors; examples of studies of inorganic powders (e.g., H_2O_2 , metal powders, etc.) can be found in the book of Rosencwaig (2). Very practical applications of PA spectroscopy can be found in the investigations of diesel smoke particles by Roessler (60) and Bruce and Richardson (61).

5.2 Direct OA Generations

Although the possibility of directly generating acoustic waves in condensed matter by a modulated laser beam was pointed out by White (7) in 1963, it was not until the work of Hordvik and Schlossberg (62) that the direct-coupling OA technique was first demonstrated as useful for detecting weak absorptions in condensed matter. In their experiment, a cw laser (CO_2 , CO, Ar^+ , etc.) was used; the chopped beam is incident on a highly transparent solid sample. A piezoelectric transducer is attached on one surface of the sample with epoxy, while the other similar transducer is positioned close to the opposite surface of the sample without contact. The purpose of the latter transducer is to measure the effect of scattered laser light onto the transducers. Using laser powers of several hundred mW, and chopping frequencies of 0.15-3 kHz, Hordvik and Schlossberg (62) achieved an absorption sensitivity of 10^{-4} to 10^{-5} cm^{-1} , depending on the amount of light scattering in the solid. In a latter experiment with a similar apparatus, Hordvik and Skolnik (63) reported that surface and bulk absorptions in solids can be separately identified, because surface absorption produces a hemispherical wave, while bulk absorption produces a cylindrical wave, distinguishable by spatial and temporal characteristics.

Besides the above direct-coupling OA spectroscopy of solids, similar experiments for liquids have been performed. For example, Lahmann *et al.* (32) have demonstrated

the detection of 0.012 ppb of β -carotene in chloroform. Here, an Ar ion laser producing simultaneously the 4880Å and the 5145Å lines is used. Modulation is performed with a dual chopper so that light of periodically alternating wavelengths is incident onto the liquid. This wavelength-alternation permits a considerable reduction of the background signal due to light scattering and window absorptions. They thus achieved a detection limit of 10^{-5} cm^{-1} absorption by the solution.

All the above direct-coupling OA techniques for solids or liquids rely on the use of a chopped light beam, typically at chopping frequencies below a few kHz. Window absorptions and effects of light scattering onto the transducer are usually the origins of detection limitations, although other factors like heating of the liquid by the strong cw laser beam of power $\sim 1 \text{ W}$ (causing convection currents, self-defocussing, *etc.*), mechanical noise at low frequencies, electrical pick-up noise at multiples of line frequencies, *etc.*, also pose limitations. These limitations are minimized in the pulsed OA technique developed by Patel and Tam (64) using pulsed laser beams of low duty cycle (*e.g.*, 1 μsec , 1 mJ pulses at 10 Hz). Time-gating the desired OA signal (which travels ballistically from the illuminated region of the sample to the transducer) can be used to discriminate against window absorption (which usually arrives later than the desired OA signal) and against light-scattering (which occurs almost instantaneously, *i.e.*, earlier than the desired OA signal). Noise effects due to steady heating are minimized by using a low average laser power of $\sim 10 \text{ mW}$. Mechanical noise and electrical pick-up noises are large at frequencies $\leq 10 \text{ kHz}$, and can be eliminated by using high frequency band-pass filters (*e.g.*, passing between 0.1-0.5 MHz); this is possible because the pulsed OA signal produced by short laser pulses ($\leq 1 \mu\text{sec}$) is of

high acoustic frequencies (≥ 0.1 MHz), in contrast to the low-frequency OA signals produced by chopped cw excitation beams considered above.

5.2.1 Weak One-Photon Absorption

Similar to the gas-phase OA case, the high sensitivity available with the use of piezoelectric transducers in direct contact with the condensed sample has been utilized to measure weak absorptions. The gas-microphone PA method is seldom used for measuring weak absorptions because of the comparatively lower sensitivity, although McDavid *et al.* (65) have used it in conjunction with high intensity CO₂ laser sources to measure weak absorptions of alkali halide samples at 10.6 μm . The investigation of Tam *et al.* (66) indicates that pulsed OA spectroscopy can be used to measure weak absorption coefficients $\sim 10^{-6} \text{ cm}^{-1}$ in liquids with path lengths of a few cm by using pulsed lasers of energy 1 mJ and duration 1 μsec , and using PZT transducers that are in direct contact with the sample. An important example of such a method of pulsed spectroscopy in liquids is the measurement of the visible absorption spectrum of water by Tam and Patel (67). Water is, of course, the most important liquid in many respects (environmental, biological, technological, geological, *etc.*), and hence many workers have previously measured its absorption spectrum, mostly by using long pathlength absorption techniques. Accuracies of the previous measurements were severely limited by scattering losses at windows and in the liquid, by refractive index effects causing small changes in the collimation of the light beam through the liquid onto the detector, by contamination of the liquid due to the containing vessel, *etc.* Thus, disagreement of previously available data is as large as a factor of 10 at the "green minimum." However, the pulsed OA spectroscopy method of Tam and Patel (67) avoids the above-mentioned limitations, and provides what is believed to be the most

reliable absorption spectra in the visible range for pure ordinary water as well as for heavy water in room temperature.

5.2.2 Trace Detection

The use of direct OA spectroscopy for trace detection in liquids *e.g.*, by Lahmann *et al.* (32), has been mentioned earlier. Obviously, for routine measurement of trace constituents in a liquid, a cell that is not vulnerable to contaminations and corrosions is desired, and such a cell is described by Tam and Patel (68). Another design for trace analysis is a flow-through cell described by Sawada *et al.* (69) who have used it to detect carcinogenic dyes in solutions. Such flow-through OA cells, in conjunction with pulsed or suitably-modulated cw lasers, should be quite valuable for continuous real-time sampling of liquids. A new flow cell, suitable for OA detection as well as for other modes of detection simultaneously, has been described by Voigtman and Winefordner (70).

5.2.3 Thin-Film Absorptions

The monitoring of surface absorption or thin-film absorption is one of the most powerful applications of OA spectroscopy. Important examples include absorptions by glass surfaces, laser mirror coating, and thin-film chromatography plates. Some of the earlier important work can be found in the series of papers by Nordal and Kanstad (71,72). In their work, various substances and complexes on metal surfaces are investigated. This may have important applications for surface chemistry and surface catalysis on metal surfaces. Such surface reactivity studies are best studied by infrared (IR) photoacoustic spectroscopy (to probe vibrational transitions) as shown by Low and Parodi (73). Pulsed OA detection has been used to measure absorptions due to a thin film of powdered sample (Tam and Patel (74)), or due to a liquid film of several micron

thickness trapped between substrates (Patel and Tam (75)). In more recent developments, Coufal and co-workers (76,77) have demonstrated OA spectroscopy of adsorbed molecules by using an infrared modulated laser beam and a PZT transducer onto which a silver substrate layer and an adsorbing gas (e.g., NH_3) are deposited under ultra-high vacuum conditions. OA spectrum of sub-monolayer surface molecule layer can be detected. Coufal *et al.* (77) also show that by using polarization modulation instead of the previously employed intensity modulation, the background signal originating from the absorption of light by the substrate material can be dramatically reduced. Intensity fluctuations of the exciting light source are cancelled, thus improving the detection sensitivity for the adsorbate considerably. In the case of ammonia on silver films, a few thousandths of a molecular monolayer can be detected without intensity stabilization of the light source.

5.2.4 Nonlinear Optical Absorptions

In nonlinear spectroscopy, the absorption is usually detectable only when high intensity light sources (like pulsed lasers) are used. Hence, the pulsed OA technique developed by Patel and Tam (64) is ideally suitable for measuring weak nonlinear optical absorption/emission effects, e.g., Raman scattering or multiphoton absorption. The first demonstration of OA Raman-gain spectroscopy (OARS) for liquids was reported by Patel and Tam (78). Two synchronized flashlamp-pumped dye lasers are used to provide the pump and the signal pulses, and gated OA measurement with a boxcar integrator is used to detect the energy deposited in the liquid due to the stimulated Raman scattering. The measurement of weak two-photon absorption cross-sections by an OA method was also demonstrated by Tam and Patel (79). Previously, sound generation in liquids due to two-photon absorption was known, but

the effect had never been applied for quantitative measurements of two-photon cross sections. Another important example of OA monitoring of two-photon absorption in insulators or semi-conductors is the work of Van Stryland and Woodall (80) who have reported measurements of two-photon absorption in CdTe and CdSe using pulsed dye lasers and piezoelectric transducers coupled to the sample with a suitable liquid.

Other developments in nonlinear OA spectroscopy in condensed matter include the use of very short laser pulses to study excited state lifetimes. The sample is excited by two short laser pulses that are temporarily separated. The first laser pulse produces certain excited states, and the second laser pulse that can be controllably delayed from the earlier one by time t_d causes further excitation of the excited states. Thus, the OA signal depends on t_d , and this dependence provides the excited state lifetimes. This stepwise delayed excitation is first done by Rockley and Devlin (81) using nanosecond laser pulses, and is much improved in time resolution by Bernstein *et al.* (82) and by Heritier and Siegman (83) with the use of picosecond laser pulses.

6. DISCUSSIONS AND SUMMARY

The technique of OA spectroscopy relies on the production and detection of acoustic waves due to a modulated excitation light beam. As the wavelength of the excitation beam is scanned, the magnitude of the acoustic wave or pulse changes, and thus an excitation spectrum commonly called an OA or PA spectrum is obtained. The phase or shape of the acoustic wave or pulse may provide additional information on the thermal properties or excitation lifetimes of the sample. Important advantages of OA spectroscopy are zero-background, high sensitivity, applicability to difficult samples, ^{depth-profiling capability,} simplicity, and the detector being "ultra-panchromatic" (*i.e.*, useful for any excitation wavelength).

The meaning of the term "opto-acoustic spectroscopy," as generally understood and as used in this article is a technique using light-induced sound-generation for *optical* spectroscopy. Since the opto-acoustic effect involves optical and acoustical waves, we may also expect an "opto-acoustic spectroscopy of the second kind," (OAS II), which is a technique using light-induced sound-generation for *acoustical* spectroscopy. This has recently been demonstrated by Tam and Leung (84) in gases. Their technique relies on the use of a short-duration laser pulse to generate reliably a narrow acoustic pulse containing a broad Fourier frequency spectrum; as this pulse propagates, the various Fourier components are absorbed differently, resulting in a pulse distortion that is probed by a focused CW laser beam. Fast Fourier transform of the transient probe deflection signal provides the acoustic absorption spectrum; this is much faster than conventional acoustical spectroscopy which involves transducers for generation and detection, and point-wise frequency measurement. This new technique of OAS II, which is all-optical and non-contact, represents a new analytical application of lasers, which generate and probe acoustic pulses in a medium to obtain important properties related to acoustic propagations like compositions, temperatures and inelastic collisions.

The concept of OA spectroscopy in its generalized form (*i.e.*, including other types of acoustic generation mechanisms and other types of incident energetic beams) is reviewed in Fig. 3. The incident beam can be electromagnetic radiation in the visible or near-visible range (as is the case in most OA studies) or in other spectral regions from RF to X-rays; it can also be a particle beam of electron, proton, muon, neutrino, *etc.* Several investigations describing acoustic generation by nonoptical beams have been reported in the literature, *e.g.*, Melcher (85) has reported the acoustic detection of RF absorption in electron paramagnetic resonance and Learned (86) has discussed the

acoustic detection of energetic particles (cosmic ray muons or neutrinos) in deep oceans. To cause acoustic generation, the incident beam can be pulsed, or modulated at close to 50% duty cycle; as shown in Fig. 3, the corresponding OA signal is a transient acoustic signal with a well-defined delay time, or a modulated acoustic signal with a well-defined phase-shift. Typically, the magnitude of the OA signal provides a measure of the energy or intensity of the incident beam, while the delay time or phase-shift provide information on the acoustic propagation time or the de-excitation time in the sample. It is now obvious that the acoustic detection techniques discussed are not only useful for optical spectroscopy, but can also be advantageously used to detect many types of energetic beams, and study their interactions with matter.

In this article, we have mainly been concerned with the technique of OA spectroscopy based on the thermal expansion OA generation mechanism. We have already indicated that other OA generation mechanisms are also possible. This means that many other interesting effects can be studied by OA monitoring; for example, chain reactions in photochemical reaction can cause strong acoustic amplifications (Diebold and Hayden (87)); weak laser pulses of 1 mJ energy can generate an acoustic shock wave (via breakdown in a vapor) that is observable many cm away from the breakdown region (Tam *et al.* (27)); and micro-mechanical motions in the form of droplet ejection from a nozzle can be controlled by pulsed OA generation (probably involving boiling) in liquids (Tam and Gill (88)). Furthermore, ultra-short acoustic pulses of duration ≤ 1 nsec can be generated for new ultrasonic testing of materials (Tam (89)). The study and applications of these various OA generation mechanisms in different systems will be an area of fruitful research.

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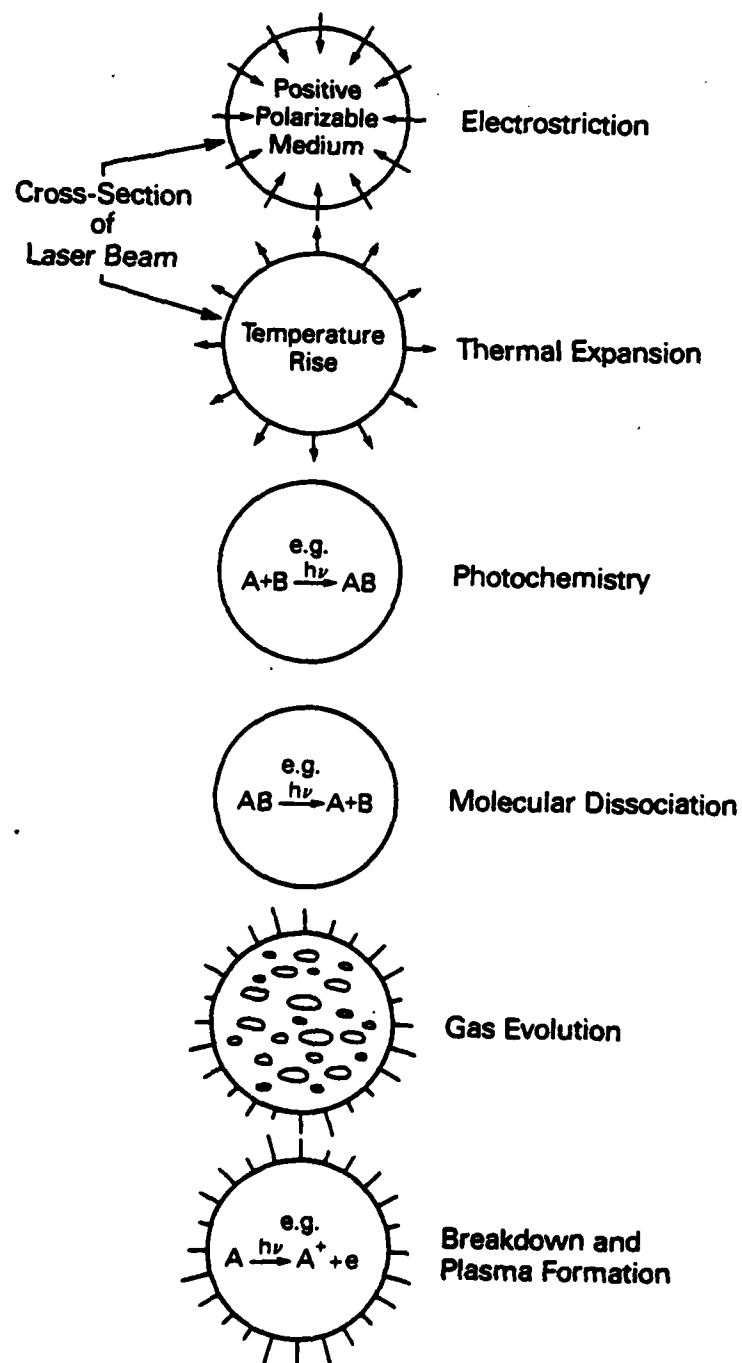


Figure 1. Some common mechanisms of OA generation. The technique of OA spectroscopy almost always use the thermal expansion mechanism.

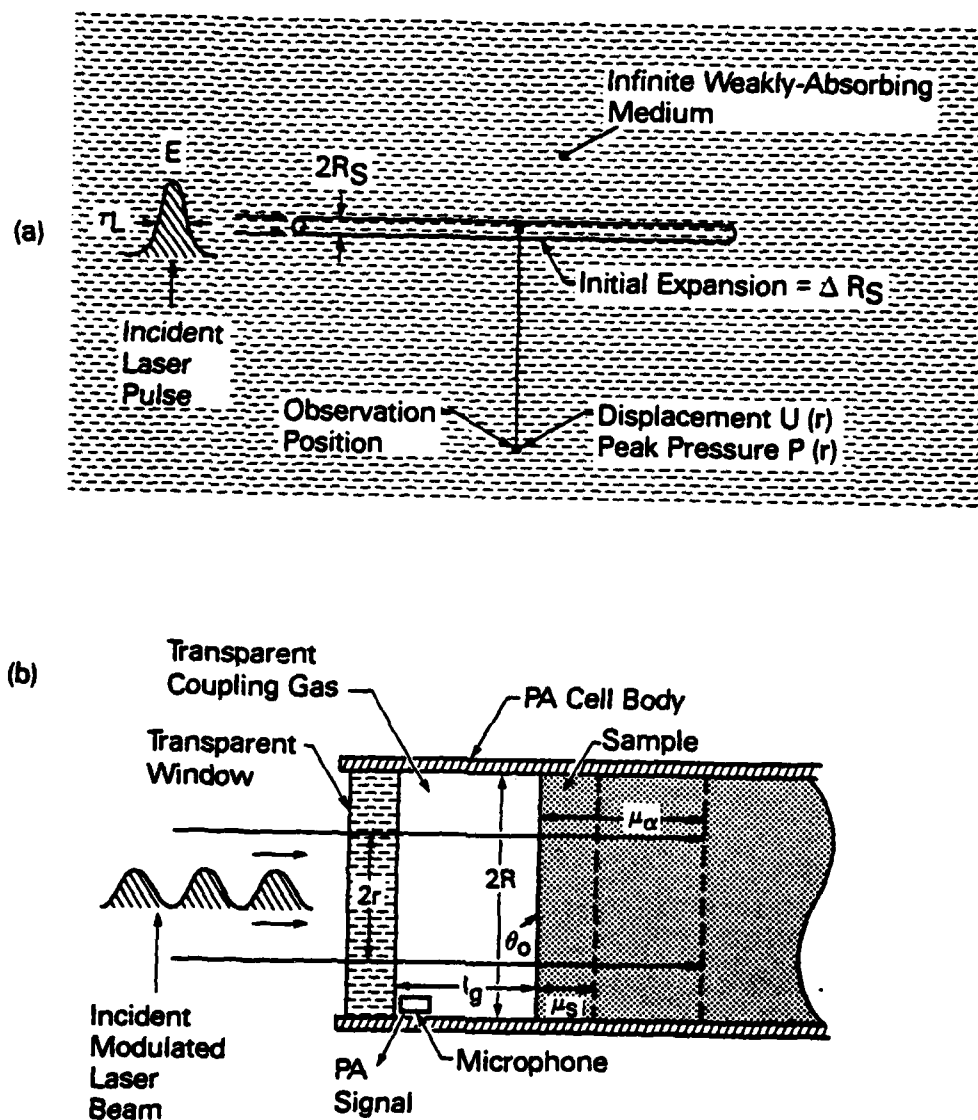


Figure 2. Schematic explanation of the two cases of thermal OA generation, direct (a) and indirect (b). For clarity, we simply use "OA" to refer to direct acoustic generation as exemplified in (a) and use "photo-acoustics" (PA) to refer to indirect acoustic generation in a transparent coupling fluid as exemplified in (b).

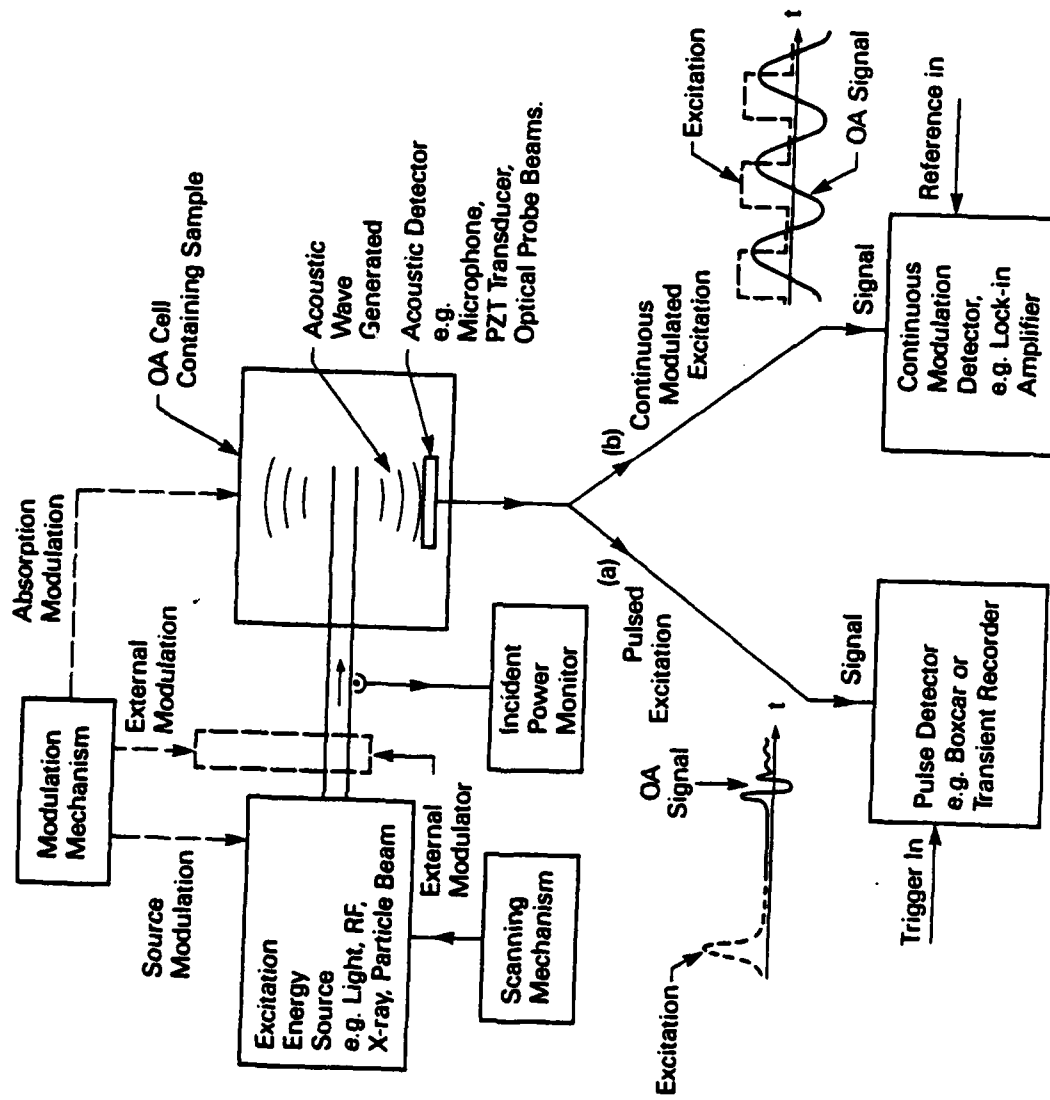
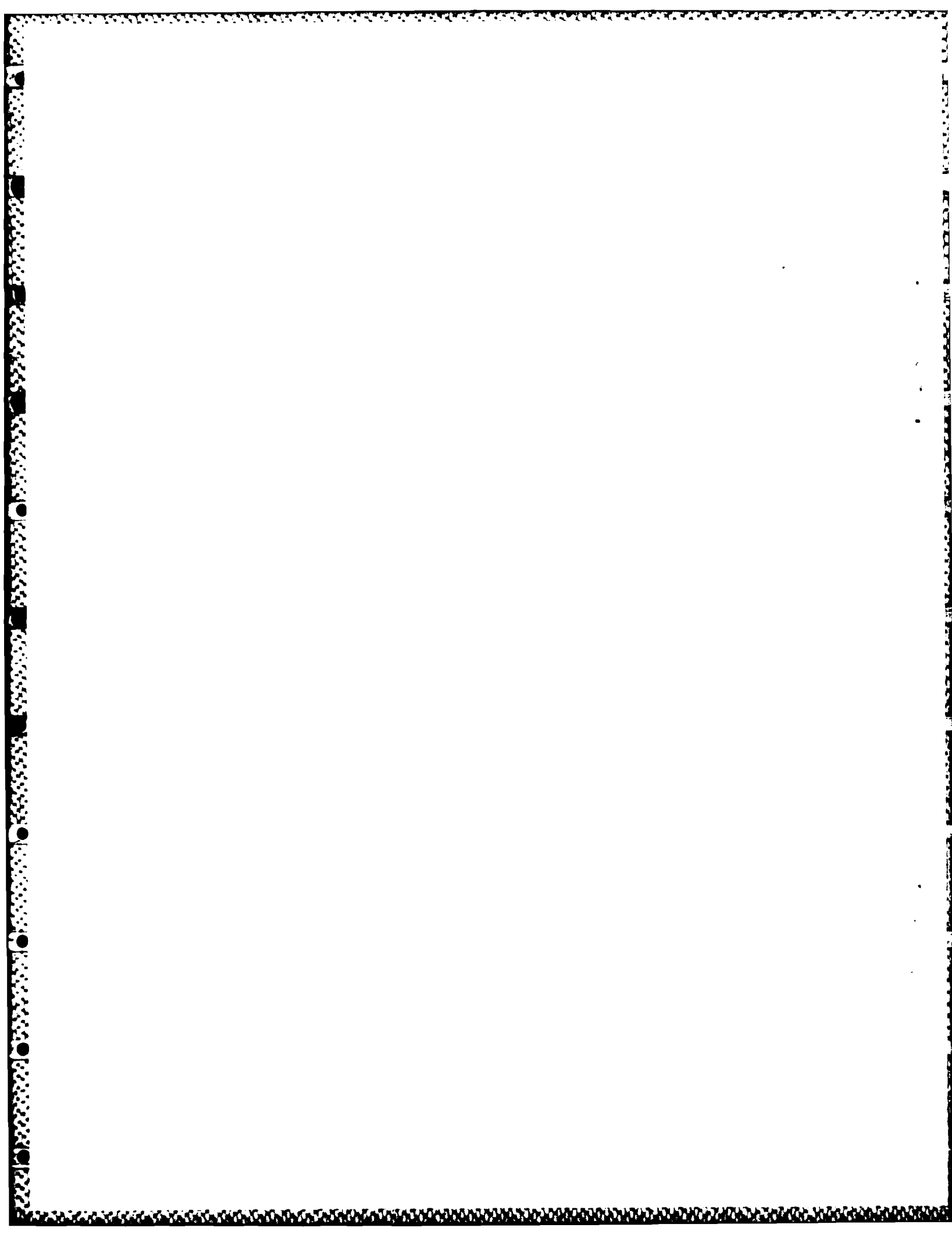
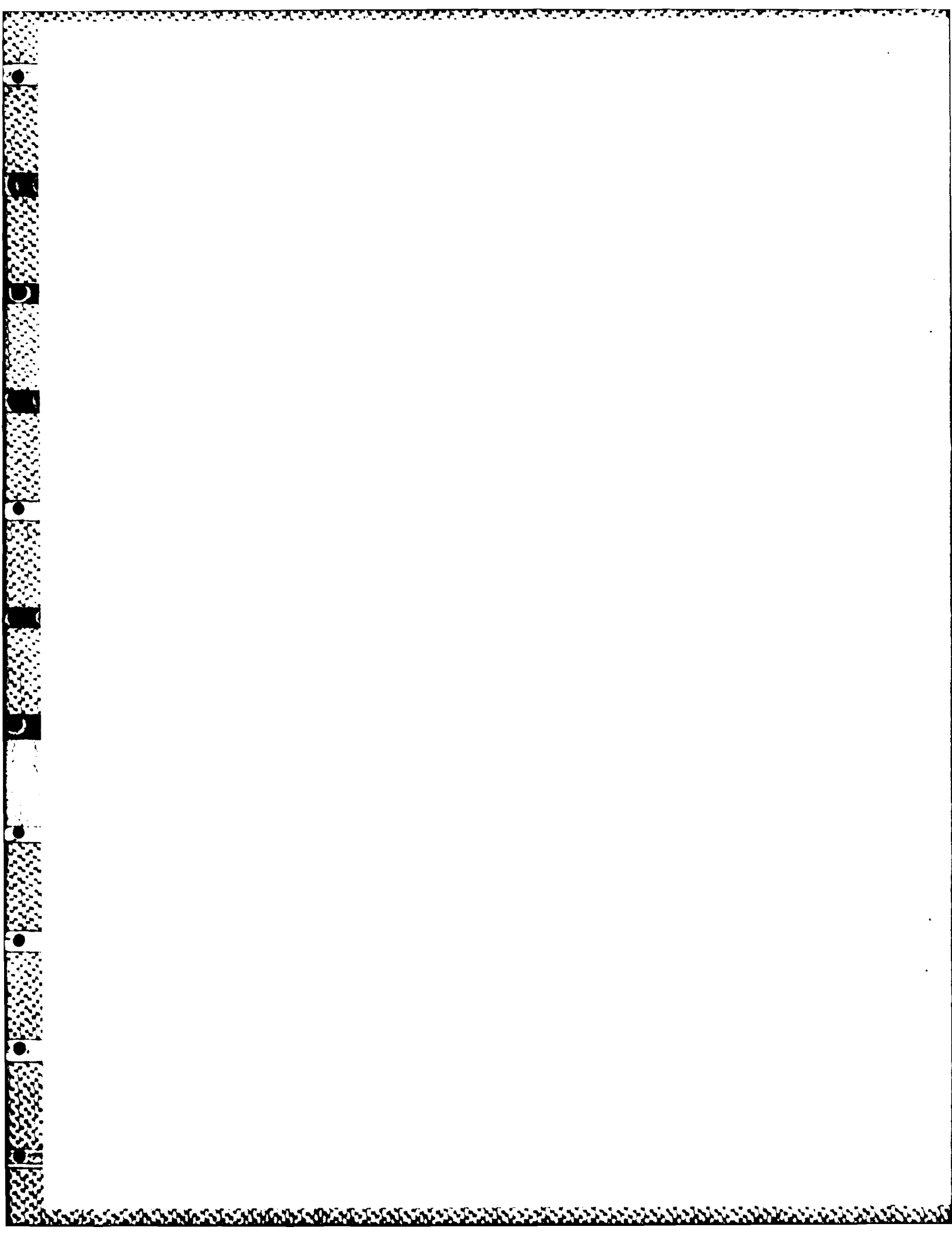


Figure 3. The generalized OA effect.



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